PYROLYSIS OF COAL WITH HYDROGEN ATOMS

J. Bi, T. Kamo, Y. Kodera, H. Yamaguchi, and Y. Sato

Energy Resources Department,
National Institute for Resources and Environment
16-3 Onogawa, Tsukuba-city, Ibaraki, 305-8569 Japan

Keywords: coal hydropyrolysis, hydrogen atom, low pressure

ABSTRACT

The reactions of coal directly with hydrogen atoms are very important for understanding the mechanisms of coal liquefaction and coal hydrogasification. In the present study, Taiheiyo coal was reacted in a low pressure TG with hydrogen atoms(induced by microwave discharge cavity) and hydrogen gas under a pressure range of 1.0 - 50.0 torr, and a temperature range of 20 -1000℃, with heating rates of 5-20 ℃/min. The yields of char, gas and liquid were measured and analyzed by TG-MS and GC-MS respectively. The results showed that the conversion of coal with hydrogen atoms was higher than that under low pressure of hydrogen gas. More liquid and gas products were obtained in the reaction with hydrogen atoms. It was observed that in the presence of hydrogen atoms, CO was more produced at a relative low temperature. Alkylated naphthalene compounds in the liquid yield were less produced in the reaction with hydrogen atoms than in the atmosphere of hydrogen gas.

INTRODUCTION

It is recognized that reactions of coal hydropyrolysis has a significant effect on the yield and distribution of end products such as coal-derived liquids, gases, coke, or pollutant emissions in the processes of coal liquefaction and coal hydrogasification under various conditions. In usual coal hydropyrolysis, thermal decomposition of coal occurs first and tar and some light carbonhydrogen compounds release at/around 400-500 ℃. After the temperature is increased to that hydrogen decomposes, then the hydrogen atoms react with coal, coal-derived pyrolysates and char, yielding products with a rather wide molecular distribution. Therefore the mechanism in hydropyrolysis is much more complex comparing with in pyrolysis. To investigate the reactions of coal directly with hydrogen atoms are very important for understanding the mechanism of hydropyrolysis. However, the information on reaction of coal directly with hydrogen atoms is limited. Amano et al.[1] investigated reactions between carbonized coal and hydrogen atoms using a discharge flow apparatus in a temperature range of 130-250 ℃ under 1Torr pressure. They found that oil yielded in the presence of hydrogen atoms has a different composition from that in the absence of hydrogen atoms , while a similar composition with that of middle fraction of petroleum distillate. In their another study[2], it was found that the liquid products contain more monocyclic alkanes, which is rather different from the liquid products yielded in conventional coal liquefaction. In addition, the liquid products contain little compounds of heteroatoms.

Hydropyrolysis require more detailed chemical information to predict the distribution of final products. Especially the reactions of coal directly with hydrogen atoms are needed to be further investigated under a wide conditions. The present study investigated coal reactions in the presence and absence of hydrogen atoms by means of vacuum TG/MS. Gas components of CH_4, CO and CO_2 were quantitatively measured and their variations with temperature were observed. The liquid products obtained at different temperatures were analyzed and compared in different atmospheres.

EXPERIMENTAL

A vacuum thermogravimetry(TG, Rigaku, Thermo plus TG8120) was used to observe the variation of coal weight, as shown in Figure 1. About 4.0 mg(-100 mesh) of Taiheiyo coal was placed in a quartz pan(ϕ5mm) which was inserted into a quartz tube reactor. The pan was heated from ambient temperature to 1000 ℃ at a linear heating rate of 5 ℃/min. The oven temperature was measured and controlled at the bottom of the pan by using a thermocouple. The pressure in the TG balance chamber was evacuated and controlled at less than 1.0 torr by a rotary vacuum pump and an adjustable valve.

Ultimate analysis data of Taiheiyo coal are 74.1 C, 6.4 H, 1.3 N, 18.0 O (by difference), 0.2 S(wt%, daf) and 14.2% ash(dry base).

Hydrogen gas was introduced to the TG chamber at a flow rate of 1.0cm^3/min(standard temperature and pressure, STA). Hydrogen atoms were induced by passing hydrogen gas through a microwave discharge cavity(2450 MHz). The discharge cavity was located at an introduction tube which was 10cm above the quartz reactor. Total distance between the discharge cavity and the coal sample was about 20cm which ensured the influence of plasma and UV from the discharge on the coal sample could be negligible. To prevent recombination of the hydrogen atoms, boric acid solution was coated in the inner surface of the reactor. For comparison, helium gas was also used under the same conditions as hydrogen gas was used.

The produced gas were analyzed by a mass spectrometer(MS, Balzers QMG112A). A turbomolecular pump(Balzers TMH/U 260) was used for evacuating the MS chamber up to 10^{-7} torr. MS conditions were set as follows: electron ionization voltage 70eV, mass range scanned 1-110 amu, scan sweeping time 52s. Each spectrum scanned was recorded and stored by computer through a MS interface(VTI, Areo Scan 1600MS/RGA).

Argon gas at a flow rate of 0.01 cm^3/min (STA) was used as internal standard. Relation between ion intensity and flow rate of CH_4, CO and CO_2 was calibrated. Therefore the gas products could be quantitatively measured through the ion intensity ratios of argon to CH_4, CO and CO_2. Before the experiment began, the background ion intensity was recorded and then subtracted during data treatment.

The liquid products were collected in a sample tube packed by Tenax powder. The sample tube was inserted in a U-tube immersed in a dryice trap. Using a flash thermal desorption cold trap injector, the liquid products were analyzed by a gas chromatography(GC, HP-6890).

RESULTS AND DISCUSSION

1) Coal conversion

Coal weight variations with temperature in different atmospheres are described in Figure 2. It can be seen that the differences of weight variations in hydrogen gas, helium gas and discharged helium gas atmospheres are not so significant, where the weights decrease rapidly at around 400 ℃ and the coal conversions at 800 ℃ are about 50%. It reflects that hydrogen gas almost does not affect the pyrolysis reactions under low pressure. It also reflects that the discharge has scarce effect on pyrolysis in the present experiment, comparing the profiles between in the helium gas and in the discharged helium gas. However, the weight decreases rapidly at around 300 ℃ in the hydrogen atom atmosphere and remarkable higher coal conversion, more than 60% at 800 ℃, is observed with temperature increase. This result suggests that hydrogen atoms promote significantly the pyrolysis reaction at a lower temperature.

2) Gas products

CH_4, CO and CO_2 gas yield rate profiles with temperature in the absence and presence of hydrogen atoms are shown in Figure 3. In the hydrogen atmosphere, as shown in Figure 3(a), CH_4 reaches the maximum at around 500 ℃, CO has an increase tendency with temperature and CO_2 increases to the maximum before 400℃ then decreases. In the reaction with hydrogen atoms, as shown in Figure 3(b), the profile patterns are quite different comparing with Figure 3(a). CH_4 has two peaks at around 200℃ and 400℃. In particular, CO has a sharp increase at 200 ℃ then a small peak at 400 ℃. CO_2 increases to the maximum at 200 ℃ then decreases.

Mechanism is not exactly understood why CO increases so much. It is not likely that the shift reaction should be responsible for much CO yielded, since CO_2 increases not so dramatically as CO in the present experiment. The clarification of the mechanism is needed.

3) Liquid products

Figure 4 shows total amounts of BTX or monocyclic hydrocarbon compounds obtained at different temperatures in the absence and presence of hydrogen atoms. It can be seen that the amounts in the reaction with hydrogen atoms are much more than those in the hydrogen atmosphere with temperature increase. Comparing the amounts at 400 ℃ and 600 ℃ in different atmospheres, the amount increases about 5 times at 400 ℃ while about 2 times at 600 ℃. Combining the gas yields produced before 300 ℃ as shown in Figure 3(b), this reflects partly that why coal weight decreases rapidly at 300 ℃ in the reaction with hydrogen atoms as shown in Figure 2. It can also be seen that relatively more BTX compounds are produced at 800℃ in the reaction with hydrogen atoms. From the liquid product distribution, more monocyclic compounds and less naphthalene compounds were yielded in the reaction with hydrogen atoms than in the hydrogen atmosphere.

In the reaction of coal with hydrogen atoms, it was observed that tar was less produced comparing with in hydrogen atmosphere under the same condtions.

Exact amount of hydrogen atoms generated are not known. It was estimated[1] about 10% of the hydrogen was in atomic state near the discharge cavity when 2450 MHz microwave discharge was applied. Even less amount of hydrogen atoms exist, the impact on the pyrolysis is profound from the present experiment.

4) Effects of pressure and heating rate

Pyrolysis was also carried out in a wider experimental conditions in the hydrogen atmosphere. Increasing the pressure from 1 torr to 10, 20 and 45 torr showed a decrease in gas products. Increasing the heating rate from 5 ℃/min to 10 and 20 ℃/min resulted in an increase in gas products. It implies that the effect of heating rate on the gas products of small molecules is probably different from the effect on the larger molecular compound products(amu values larger than 50) as observed by Yun et al.[3] where they found that the pyrolysate distributions of primary pyrolysis reactions in Pittsburgh No. 8 coal are independent of heating rate over a magnitude of 10^{-2}-10^{4} ℃/s when monitoring the 50-200 amu mass range.

CONCLUSIONS

Pyrolysis of Taiheiyo coal in the reaction with hydrogen atoms was investigated and compared with pyrolysis in the hydrogen atmosphere. The result showed that the conversion of coal with hydrogen atoms was higher than that with hydrogen gas, and more liquid and gas products were obtained in the former case. It was observed that in the presence of hydrogen atoms, CO was more produced at a relative low temperature. More monocyclic compounds and less naphthalene compounds were yielded in the reaction with hydrogen atoms than in the hydrogen atmosphere.

REFERENCES

1) Amano, A., Yamada, M., Shindo, T., Akakura, T., Yotsusuji, S., Inst. of Chem. Soc. of Jpn, 1984, No. 10, 1648-1655

2)Amano, A., Yamada, M., Shindo, T., Akakura, T., Fuel, 1984, Vol. 63, May

3) Yun, Y., Maswadeh, W., Meuzelaar, H.L.C., Simmleit, N., Schulten, H.R., Energy & Fuels, 1991, 5, 22-29

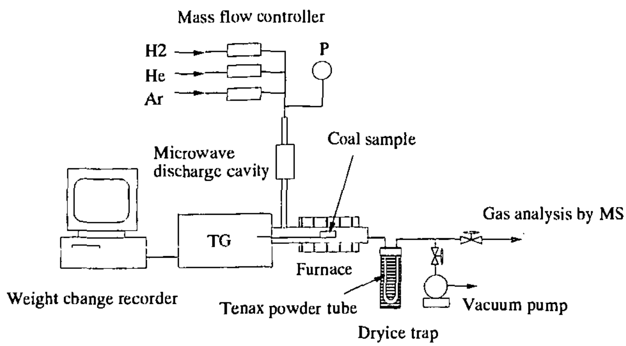


Figure 1. Experimental apparatus

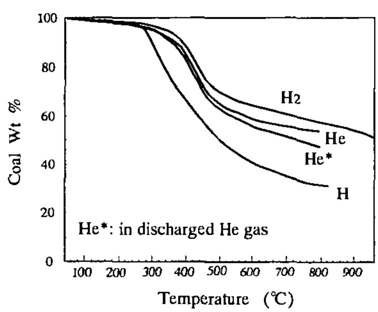


Figure 2. Coal weight decrease with temperature in various gas atmospheres

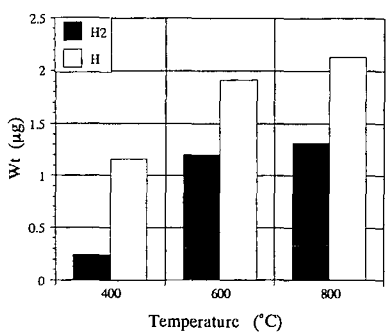
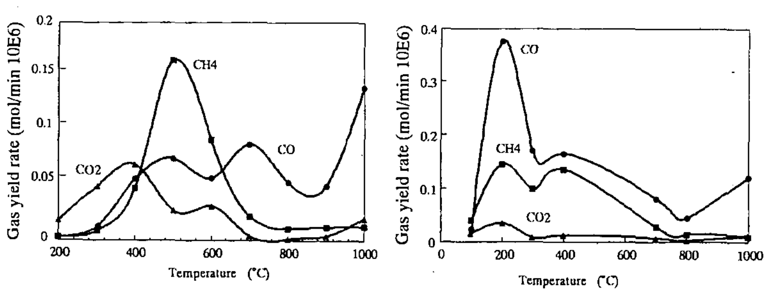


Figure 4. Weight variation of BTX compounds with temperature



(a) In H2 atmosphere

(b) In H atmosphere

Figure 3. Main gas yield rate with temperature